

- V. "On the Compounds of Ammonia with Selenium Dioxide."  
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MACALLAN, F.I.C. Communicated by Professor DEWAR,  
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The following experiments were undertaken with the object of determining the action of ammonia upon selenium dioxide. They have resulted in the discovery of two new compounds, which, from what has been ascertained regarding their constitution, may, perhaps, be best designated by the term *selenosamates* or ammonium salts of an acid—selenosamic—yet to be isolated.

*Preparation of Neutral Ammonium Selenosamate.*

Ammonia, which had been carefully dried by passing through a series of potash tubes, was led into a solution of selenium dioxide in absolute alcohol. After being absorbed for some time, minute crystals commenced to deposit, and when complete precipitation had taken place, the liquid portion was filtered off, the crystals washed with alcohol, and dried over sulphuric acid in a vacuum.

The compound formed as above described is a deliquescent salt, which separates from its solution in alcoholic ammonia in minute, but very well-defined hexagonal prisms and pyramids—both forms often occurring in combination. It is a very unstable substance, continuously liberating ammonia, and tending to the formation of a more stable acid salt. Some of the crystals which had been placed in a large stoppered bottle were found after some weeks to be entirely converted into large crystals of the acid salt. It also loses ammonia when treated with alcohol or water; and when its aqueous solution is evaporated in a vacuum, crystals of the acid salt remain. When heated, it is at once converted into the acid salt. On account of its instability, it is best prepared in a partial vacuum, and when dried placed in a stoppered bottle, which should be quite full and kept in a cool place. In this way it may be preserved of definite composition for a considerable time. It is with difficulty, and only partially, converted into ammonium selenite by the action of water upon it. When barium chloride is added to its neutral aqueous solution, only a faint cloudiness is produced, until it is heated, when a slight precipitate forms, but even after standing for weeks and long-continued boiling, only a portion of the selenium precipitates. Addition of excess of ammonia to the solution, however, precipitates a basic barium salt. It is but sparingly soluble in cold alcoholic ammonia. 1·6658 gram of solution from which crystals had deposited, left a residue of 0·0134 gram, reduced to acid salt, which is equivalent to a solubility

of one part in 116 at 12°. Heated with the alcoholic ammonia it dissolves freely, but on cooling, the solution remains long supersaturated, crystals continuing to deposit for several days. It is very slightly volatile at ordinary temperatures, both in a vacuum and in a current of air. As might be expected, potash at once liberates ammonia from it. Sulphurous acid and stannous chloride reduce it with separation of selenium. It is only slightly affected by hydrochloric or nitric acid in the cold, but strong sulphuric acid reacts violently upon it, a portion of the salt being sublimed by the heat evolved. Chlorine passed through its aqueous solution converts it completely into ammonium selenate,—a reaction which was taken advantage of for its analysis. 0.7820 gram was dissolved in water, saturated with chlorine, and barium chloride added. The resulting barium selenate weighed 1.5150 gram, equivalent to a percentage of 76.84 of selenium dioxide. The ammonia was estimated by Kjeldahl's process, slightly modified on account of the volatility of the substance. 0.5651 gram was mixed roughly with potassium permanganate in a small strong flask by means of a glass rod, after which a thin tube containing 10 c.c. of sulphuric acid mixture was lowered into it, and broken by shaking the flask after it had been well secured with an india-rubber cork. It was then heated to 150° for one hour in a paraffin bath. The contents of the flask distilled with potash yielded 0.13175 gram of ammonia, equivalent to a percentage of 23.32. The results obtained agree with the composition—



	Calculated.	Found.
SeO <sub>2</sub> .....	76.53 .....	76.84
NH <sub>3</sub> .....	23.47 .....	23.32
	<hr/> 100.00	<hr/> 100.16

The original alcoholic solution from which the crystals had deposited, was found to contain selenium. In order to ascertain in what form it existed, a portion of the solution was evaporated to dryness in a vacuum. The residue weighing 0.666 gram, treated as before, yielded 1.285 gram of barium selenate, equivalent to 76.53 per cent. of selenium dioxide, the theoretical amount in the above compound, showing that a portion remained in solution after the crystals had deposited. It was considered a matter of interest to ascertain how much of the nitrogen in this salt would be precipitated by platinum chloride. 0.5772 gram was accordingly taken, platinum chloride poured upon it, alcohol added, and the mixture allowed to stand in the cold. The double chloride obtained weighed 1.5502 gram, equivalent to a percentage of 20.59 of ammonia. A second estimation in

which 0.4153 gram was taken, yielded 1.1206 gram of the double chloride, equivalent to 20.69 per cent. of ammonia. In a third estimation, 0.3835 gram was evaporated down with platinum chloride, but the double chloride obtained, 1.0237 gram, showed a rather smaller percentage of ammonia, namely, 20.52. The mean of the first two results, 20.64, is equal to 87.94 per cent. of the total ammonia, and indicates that in addition to the basic nitrogen, about three-fourths of the nitrogen contained in the radical of the salt is precipitated by platinum chloride.

*Preparation of Acid Ammonium Selenosamate.*

A solution of the neutral salt in absolute alcohol was boiled down on the water-bath until crystals were deposited. The liquid portion was then drained off, and the crystals washed with alcohol, and dried in a vacuum. On examination, they proved to consist of an acid salt. It was also found that exposure of the neutral salt in a vacuum over sulphuric acid for thirty hours was sufficient to convert it into the same acid compound. A portion of the salt obtained in the latter way was submitted to analysis. For estimation of the selenium, 0.2 gram was dissolved in water, saturated with chlorine, and precipitated with barium chloride. The resulting barium selenate weighed 0.409 gram, equivalent to a percentage of 81.11 of selenium dioxide. In a second estimation, 0.4268 gram yielded 0.8761 gram of barium selenate, equivalent to 81.42 per cent. of selenium dioxide. Kjeldahl's process was found to be unsuitable in this case for estimating the ammonia, the amount yielded by it being much too low, although a very high temperature was maintained for a considerable time. Combustion with soda-lime also gave insufficient results, owing to a portion of the substance being decomposed by the heat employed, with evolution of nitrogen. Somewhat better results were obtained by Dumas' process: 0.4035 gram yielded 49.9 c.c. of nitrogen at 12° and 771.6 mm., equivalent to a percentage of 18.09 of ammonia. An estimation of the selenium in the dried crystals was also made: 0.1523 gram yielded 0.3134 gram of barium selenate, equivalent to 81.62 per cent. of selenium dioxide. The results thus obtained agree with the formula  $3\text{NH}_3, 2\text{SeO}_2 = \text{NH}_4\text{H}(\text{SeO}_2\text{NH}_2)_2$ .

	Prepared in vacuum.			Crystallised from alcohol.		Calculated.
	1.	2.		3.		4.
SeO <sub>2</sub> .....	81.42	81.11	....	81.62	....	81.30
NH <sub>3</sub> .....	18.09	—	....	—	....	18.70

The salt thus obtained is deliquescent, and easily soluble in alcohol, from which it separates in large prisms. 2.0270 grams of saturated solution left a residue weighing 0.1191 gram, showing a solubility of

one part in sixteen of absolute alcohol at 14°. No hydrate was obtained by evaporating its aqueous solution, but the same crystalline forms were deposited as from alcohol. With barium chloride it behaves similarly to the neutral salt, a partial precipitation taking place only with difficulty. It possesses much greater stability than the neutral salt, but like the latter it is reduced by sulphurous acid and stannous chloride, and oxidised by chlorine. Potash decomposes it with evolution of ammonia, but hydrochloric, nitric, or sulphuric acid has only a slight action upon it in the cold. Kept in a vacuum or in a current of air, it is appreciably volatile at ordinary temperatures. When heated strongly, a portion of it sublimes unchanged, part of it is converted into ammonium selenite, while the remainder is decomposed into ammonia, water, nitrogen, and a residue of fused selenium. In order to estimate the amount of ammonia precipitated by platinum chloride, 0.3140 gram was taken, which yielded 0.6234 gram of the double chloride, equivalent to 15.26 per cent. of ammonia, the amount thus precipitated being equal to 81.60 per cent. of the total amount of ammonia in the salt.

*Relation of the Selenosamates to Sulphur Compounds.*

It is stated that a compound is formed by the action of ammonia on sulphur dioxide, but the description of its properties shows that it does not correspond with the selenosamates. The latter bodies correspond more closely with the compounds which sulphur trioxide forms with ammonia. The molecule,  $\text{SeO}_2$ , therefore, in these reactions acts similarly to  $\text{SO}_3$ , rather than to what is usually regarded as its sulphur analogue, namely  $\text{SO}_2$ .

In conclusion, we are engaged at present in the production of other selenosamates, and hope to give an account of them at an early date.

VI. "On the Logarithmic Law of Atomic Weights." By G. JOHNSTONE STONEY, M.A., D.Sc., F.R.S. Received April 16, 1888.

(Abstract.)

This memoir is divided into five sections.

Section 1.—When Newlands pointed out the dependence of the atomicity and other properties of some of the chemical elements upon the order in which their atomic weights succeed one another, and especially when this law was extended by Mendelejeff to all the elements, it became manifest that there exists a mathematical relation between a series of numbers and the successive atomic weights of the elements.